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<b>(54) Title:</b> METHOD FOR MAKING AND USING PLATINIZED MICROPOROUS CERAMIC MATERIALS  <b>(57) Abstract</b>  A method for platinizing microporous nanoparticulate ceramic metal oxide materials having a high surface area and mean pore diameter less than 100 Å produces a platinized catalyst suitable for degradation of organic compounds in the gas phase. The platinized catalyst produced according to the method retains the advantageous properties of the starting materials and exhibits greater catalytic activity than existing platinized metal oxide catalysts. The materials have a characteristic dark black color, in contrast to the gray materials known to the art, suggesting improved platinum loading.		

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5

-1-

METHOD FOR MAKING AND USING  
PLATINIZED MICROPOROUS CERAMIC MATERIALS

Field of the Invention

10 The present invention relates to the field of microporous nanoparticulate ceramic catalysts and more particularly to a method for making and using platinumized microporous nanoparticulate ceramic catalysts.

Background of the Invention

15 Contamination of ground water and soils by volatile organic compounds associated with fuel leaks and improper solvent disposal is a widespread environmental problem. One promising remedial approach is to use semiconductor-mediated heterogeneous photocatalytic oxidation to destroy such volatile organic compounds. Heterogeneous photocatalytic oxidation is also used for synthesis and in catalytic converters in automobiles.

25 Initial research in this area focused largely on volatile aliphatic halogenated organic compounds such as TCE and PCE. Several photocatalysts have been developed which are able, under well defined conditions, to achieve complete, or nearly complete, mineralization of such compounds.

30 Recently, attention has shifted to the more difficult to degrade compounds, particularly aromatic compounds such as benzene, chlorobenzene, toluene,

-2-

phenol, chlorophenols, and benzoic acid. Typically, the catalysts employed in efforts to remediate contamination by aromatics are heterogeneous photo-assisted catalysts in the form of semiconductor  
5 powders dissolved in aqueous suspension. Titanium dioxide powders (e.g., Degussa P25) are the most widely used heterogeneous catalysts for photocatalytically oxidizing aromatic compounds. When  
10 a suspension of titanium dioxide powder is illuminated with UV light, many aromatic compounds are converted to other compounds. In some cases, complete mineralization of the aromatic compound to carbon dioxide and water has been achieved in the gas phase  
15 under conditions of high temperature and long reaction time.

One way to increase the efficiency of titania photocatalysis is to provide a catalytic metal, generally platinum, at the surface of the titania material. Existing platinized titania catalysts are  
20 titania powders (particle size 125 microns-150 microns) with platinum in the range of 0.5-10% by weight. Using certain platinized titania materials as photocatalysts, photodecomposition of aqueous solutions of benzene to carbon dioxide as the final  
25 product, with several other minor by-products has been reported.

However, there is much room for improvement in both the catalytic materials and the catalytic photodegrading processes for complex organic  
30 compounds, both aromatic and aliphatic. One shortcoming of existing systems is that complete mineralization requires relatively long reaction times. In addition, a filtration process is required after a liquid phase reaction is complete to separate  
35 the solid photocatalyst powder from the reaction mixture. Perhaps the most challenging problem, as a practical matter, is the need to balance the desire

-3-

for maximum catalytic efficiency against the high cost of platinum metal.

Thus, it would be desirable to obtain a photocatalyst that operates efficiently using only minimal amounts of platinum that can be incorporated into a method for removing organic compounds that is rapid and does not require post-reaction separation of catalytic material.

There is also room for improvement in the processes for preparing efficient platinized metal oxide photocatalysts. Kraeutler and Bard, J. M. Chem. Soc., 100:4317-4318 (1978) described photodepositing metallic platinum on 125-150 micron particle size anatase powder. The anatase powder was suspended in hexachloroplatinic acid at pH 4, flushed with nitrogen to remove oxygen and CO<sub>2</sub>, and heated to about 55°C. Photodeposition of the platinum was achieved by irradiating the reaction mixture using an Hg-Xe lamp for 3.6 hours. The resulting platinized titania powder was described as being significantly darker than the grayish anatase powder. The distribution of platinum on the resulting material was described as fairly uniform and no agglomerates were detected by SEM. However, Kraeutler and Bard went on to note that metal deposition probably only occurs near sites where photons strike the surface and the light flux can be made very small. Thus, one would expect to find small clusters of the metal on the external support surface. Moreover, this process requires high temperature treatment to disperse the platinum on the surface without forming large aggregates. Also, the system deposits on the reactor wall in the path of incident light, resulting in waste and unnecessary expense. Platinum so deposited can ultimately largely prevent light from reaching the catalyst, further reducing the deposition efficiency.

-4-

Izumi et al., later characterized the titania powders platinized by Kraeutler and Bard as containing 10% platinum by weight, which would suggest a prohibitively high cost for the catalyst in a commercial setting. Izumi et al. demonstrated photocatalytic decomposition of benzene and aliphatic hydrocarbons in the liquid phase using these materials. Later, Izumi et al. reported the use of the same platinized titania powders to photo-oxidize benzoic acid and to photocatalytically decompose adipic acid, also in the liquid phase.

A second method used to deposit platinum on a titania powder uses high-temperature reduction of a platinum precursor in H<sub>2</sub> gas. In this method, described by Pichat et al., Nouv. J. de Chim., 5:627-636 (1981), non-porous anatase powder (50 m<sup>2</sup>/g (Degussa P25) is suspended in a small amount of distilled water with hexachloroplatinic acid, evacuated in a rotating flask at 350° K for 2 hours, dried at 393° K for 2 hours, flushed with N<sub>2</sub> while raising the temperature to 573° K, reduced in hydrogen gas at 753° K for 15 hours. Finally, the powder is cooled in a nitrogen stream. The platinized titania powders produced by Pichat, et al. were reported to be 4.85% platinum by weight. The authors also reported good homodispersion and a platinum particle size of 2-2.5 nanometers, with some 1 nanometer and 3 nanometer particles also observed. These catalysts were then used in both liquid phase and gas phase reactions. However, in the gas phase, only a simple alcohol (methanol) was degraded.

Sato, J. Catal., 92:11-16 (1985) reported a photoelectrochemical platinization method wherein titanium dioxide powder was suspended in distilled water; hexachloroplatinic acid was added along with, in certain cases, a sacrificial reducing agent. The suspension was deaerated using N<sub>2</sub> gas and illuminated

-5-

using a mercury lamp having illumination wavelengths in the range of 240-400 nanometers to photod posit the hexachloroplatinic acid on the titanium dioxide powder. The resulting slurry was washed and dried at room temperature to yield a platinized titanium dioxide powder containing 1% platinum by weight. Sato noted that in the absence of the sacrificial reducing agent, the hexachloroplatinic acid disappeared from the suspension either as a result of photoadsorption or photodecomposition, but that, in any event, no platinum was deposited unless a reducing agent was added. For comparison, Sato also prepared a platinized titanium dioxide catalyst made by reducing hexachloroplatinic acid with a 0.1 M  $\text{NaBH}_4$  solution in 0.1 N NaOH, and a catalyst prepared by the method of Pichat.

Whereas the exterior surfaces of powder grains can be platinized to provide a catalytic surface, none of the existing methods can successfully platinize metal oxide materials other than powders. Existing methods for preparing platinized catalysts have various shortcomings that make them particularly inappropriate or impractical for use with high surface area, porous metal oxide materials. Although the existing methods could be applied to such materials, the expectation would be that the vast interior surface area would not be adequately coated or that the porous structure that ensures the high surface area would be lost, or both. Therefore, it would also be desirable to have a method for forming porous ceramic metal oxide platinized catalysts that is both cost-effective and compatible with high-surface area materials.

#### Summary of the Invention

The present invention is summarized in that a method for forming a platinized microporous metal

-6-

oxide nanoparticulate ceramic catalyst employs as a starting material a microporous, metal oxide, nanoparticulate catalyst characterized as having interconnected pores, a surface area greater than about 50 m<sup>2</sup>/g, and a mean pore diameter of less than about 100 Å. A platinum precursor is adsorbed onto the particles without photoillumination, for a time sufficient to achieve adsorption equilibrium. A platinum precursor is a platinum-containing compound that can adsorb to the metal oxide material and can be reduced to zero-valent platinum under reducing conditions. For example, the PtCl<sub>6</sub> ionized form of hexachloroplatinic acid is the preferred platinum precursor in the present method.

Then, the microporous catalyst with the adsorbed platinum precursor is subjected to reducing conditions at a temperature that does not affect the mean pore diameter of the micropores and at a pH that does not dissolve the catalyst, until the platinum is reduced to zero-valent platinum metal and so that a platinized microporous metal oxide nanoparticulate ceramic catalyst is formed.

The platinized catalyst is then dried at a temperature that does not affect the mean pore diameter of the material.

Materials prepared according to the method of the present invention are physically distinct from platinized powders and exhibit higher thermocatalytic and photocatalytic turnover numbers than powders prepared according to the same method. Moreover, these platinized materials are able to readily degrade and mineralize benzene, a difficult-to-degrade organic compound, in the gas phase.

#### Detailed Description of the Invention

In a first aspect, the present invention is a method for forming a platinized catalyst that solves

-7-

the identified problems and shortcomings in the art.

The microporous nanoparticulate, metal oxide ceramic starting materials for use in the platinization method can be prepared in the manner described in U.S. Patent No. 5,227,342 (Anderson and Xu), which is incorporated herein by reference. See also Xu, Q. and M. A. Anderson, J. Mater. Res. 6:1073 (1991) and Yamazaki-Nishida, S. et al., J. Photochem. Photobiol., 70:95 (1993). Instead of using roto-evaporation to prepare a xerogel, as has been described, the materials were placed in a 55°C oven for several days.

The nanoparticulate, microporous, metal oxide particles produced in the methods therein described are characterized by interconnected, rather than closed, pores with a mean pore diameter of less than 100 Å and an available surface area in excess of about 50 m<sup>2</sup>/g and as high as about 400 m<sup>2</sup>/g. In mixed oxide materials (e.g., mixed titania - zirconia or titania - silica), higher surface areas, up to about 500 m<sup>2</sup>/g, can be achieved because pores can remain open longer at higher temperatures during sintering. The surface area is preferably 100-400 m<sup>2</sup>/g. The mean pore diameter, which represents an average of pores having larger and smaller diameters, is preferably in the range of 5 - 100 Å for catalytic reactions. It has been determined by the inventors that the presence of both very small platinized pores and somewhat larger platinized pores in these materials is important to their high activity. The larger pores capture contaminants while the smaller pores trap and restrain the contaminants in place until oxidation is complete. The inventors refer to this phenomenon as "deep oxidation catalysis." The porosity of these materials is greater than about 30% and can range as high as about 60%, depending upon the preparation conditions, the firing temperature, and firing time. The metal

-8-

oxide can be any transition metal that can be formed into nanoparticulate ceramic materials, as well as other elements such as silicon and aluminum. Although titania is used in many of the examples below,

5 titania-based zirconia and silica mixed oxides are also shown to function well. It is not thought that the particular metal oxide selected is critical, but rather that the nature of the microporous surfaces are more responsible for the high quality of the

10 platinized materials. However, since titania is recognized as having superior catalytic properties, it is the preferred metal oxide. "Nanoparticulate" is intended to indicate that the metal oxide materials are formed in a sol-gel process in which discrete

15 metal oxide particles of irregular shape, sized, on average, between about 3 and 50 nm, preferably 10-20 nm, in size, agglomerate in the manner described in US Patent No. 5,227,342 to form particulate ceramic materials (as opposed to polymeric materials). The

20 presence of pores in the described size range is important for providing both high catalytic surface area in large pores, as well as sites to trap reactants in very small pores so deep oxidation processes can occur. The porous metal oxide starting

25 materials can be in the shape of pellets, films, sheets, membranes and the like. It is also possible to coat and platinize these materials on support surfaces having desired structures, such as honeycomb structures. In this application, references to

30 "pellets" are intended to encompass nanoparticulate materials in any physical form appropriate for use in catalytic reactors. When the metal oxide is titanium dioxide, as is preferred, the crystal structure of the materials formed is primarily anatase (e.g., 89%

35 anatase, 11% rutile when fired at 300°C for four hours), with the primary crystallites composing the aggregated porous metal oxide materials having an

-9-

average size of about 80Å.

The metal oxide ceramic starting materials are  
platinized according to the following methods. If the  
material is a solid membrane or an extruded product,  
5 the material is crushed or ground into granular porous  
pellets. Pellets are not intended to have a  
particular shape, but are much larger than the grains  
that comprise metal oxide powders. Granular pellets  
between 0.05 and 10 mm in either dimension are  
10 appropriate for use in the platinizing method herein  
described. The pellets can be non-uniform in size and  
shape. The pellets are size-screened by sieving and  
are selected to meet the needs of the catalytic system  
in which the pellets will be employed. A preferred  
15 range of pellet dimensions is between 0.5 and 1.4 mm.

The pellets are immersed with stirring in an  
excess of deionized water. The amount of water is not  
critical. One hundred fifty ml of deionized water is  
a suitable amount to accommodate 25 g of titanium  
20 dioxide pellets although more or less water can be  
used. The metal oxide particles should be suspended  
in clear water. If the water turns a milky white  
color when the pellets are added, the milky water  
should repeatedly be decanted and replaced with fresh  
25 deionized water until the deionized water remains  
clear.

The platinum precursor is then added to the  
immersed ceramic pellets. A convenient way to  
introduce the platinum is to add an acid comprising  
30 platinum and a halogen. Hexachloroplatinic acid  
( $\text{H}_2\text{PtCl}_6$ ) is available commercially from Aldrich  
Chemical as either a solid or as an 8% by weight  
aqueous ionic solution, and is to be considered the  
preferred acid. Either form of the acid can be used,  
35 however the solid form hydrolyzes and dissolves too  
rapidly in high humidity conditions to permit accurate  
weighing. Thus, the most preferred form of

-10-

hexachloroplatinic acid under standard open laboratory conditions is the 8% by weight aqueous solution. The appropriate amount of platinum is readily determined from the molecular weights of the reactants. The weight percent of platinum is determined relative to the weight of the metal oxide. The platinum preferably ranges as high as 2% by weight, but can be higher. The amount of platinum need not be greater than 0.5% by weight to prepare a platinized catalyst having the desired activity, and can be less than 0.3% or even 0.1% by weight. The intrinsic activity of the platinized material (measured by turnover number) does not increase after a loading level of about 0.5%. However, the apparent activity of the material (measured as extent of conversion per constant amount of material) continues to increase up to about 2%. Two percent platinum, by weight, is equivalent to 4.2% by weight of the  $\text{PtCl}_6$ -ion platinum precursor. A 0.1 weight percent platinum deposit on titanium dioxide is made by adding 0.263 ml of the 8% hexachloroplatinic acid solution per gram of titanium dioxide.

When the hexachloroplatinic acid has been added to the metal oxide catalyst, the two are allowed to react for a period of about 20 minutes to 1 hour to ensure adsorption equilibrium, at which time no additional platinum ions adsorb to the metal oxide material. Beyond about 1 hour, there is no additional benefit observed from waiting a longer time.

The adsorption of the platinum to the metal oxide pellets can be performed at room temperature and does not require UV illumination. Nor is it necessary to platinize under deaerated conditions, as has been recommended in the platinization method of Sato, J. Catal. 92:11-16 (1985).

At the end of the adsorption period, the particles are allowed to settle and the water is decanted from the reaction vessel.

-11-

Next, the platinum ions are reduced to zero-valent platinum metal. A preferred reduction method uses sodium borohydride,  $\text{NaBH}_4$ , in dilute  $\text{NaOH}$ , prepared fresh immediately before use. For  
5 convenience, the reducing agent can be prepared during the adsorption of the platinum to the metal oxide pellets. The reducing agent can be present in stoichiometric excess. The molar ratio of  $\text{NaBH}_4$  to  
10 platinum should be greater than 1. A concentration of 0.1-0.3 M  $\text{NaBH}_4$  is suitable. Higher concentrations of the reducing agent may be acceptable. The actual concentration of sodium hydroxide is not absolutely  
15 critical, although it must be sufficiently dilute (about 0.05N-0.01N) so as not to attack and dissolve the underlying metal oxide microporous particles. At 0.1N  $\text{NaOH}$ , dissolution of the metal oxide material is observed. For each gram of 0.1% by weight  
20 platinum/ $\text{TiO}_2$  catalyst prepared, 2 ml of dilute  $\text{NaOH}$  containing 0.02 g of sodium borohydride is suitable. These amounts are adjusted accordingly for differing amounts of platinized catalyst as well as for variations in the weight percent of platinum loaded.

When the reducing agent is prepared, it is added to the catalyst at room temperature. A large amount  
25 of gas evolves during the reduction, so it is strongly suggested that the addition be performed, with rapid stirring, in an exhaust hood. After about 10 minutes to one hour of rapid stirring, the liquid is decanted and the platinized catalyst is washed with deionized  
30 water several times until the  $\text{NaBH}_4$  is removed. Four washes are generally sufficient.

The platinized catalyst is then dried. It is important not to dry the platinized catalyst at a temperature that will increase the density and reduce  
35 the porosity and mean pore diameter of the metal oxide microporous platinized material. At temperatures above about 400°C, marked reductions in mean pore

-12-

diameter and porosity, and an increase in density, are observed. Drying at about 60-120°C for 1-20 hours is suitable.

5 An alternate, but related, method for preparing the platinized catalyst from metal oxide pellets is to dry the pellets at a relatively low temperature (100-120°C) for several hours, e.g. 3 hours. The 8% hexachloroplatinic acid solution is added to the dried particles at room temperature until the particles  
10 become wet incipiently. After loading, the particles are again dried under the same conditions as previously. Then, the reducing agent in solution, which is the same as in the previous method, is added to the dried particles at room temperature. Then, the  
15 liquid is decanted and the platinized particles are rinsed and dried as previously. Platinized materials prepared in this alternate method are comparable in photocatalytic properties to those of the materials that result from the preferred method.

20 The color of a platinized catalyst along a spectrum ranging from light grey to dark black can reflect the extent of platinum dispersion during loading, with more thorough dispersion being reflected in a uniformly darker color. It has been found that  
25 the microporous nanoparticulate metal oxide ceramic materials with adsorbed platinum ions can be reduced in the gas phase at about 200°C with H<sub>2</sub> gas to obtain platinized catalyst that is even darker and more uniformly black than that which results from the NaBH<sub>4</sub>  
30 reduction, without apparent loss of internal pore structure. This reduction temperature is also significantly lower than that required by prior H<sub>2</sub> reduction methods, which, it is noted, are too high to be used with the starting materials used herein. Even  
35 more unexpectedly, the H<sub>2</sub> gas reduction can also be performed at room temperature (about 20°-30°C) to obtain platinized catalyst only slightly less black

-13-

than those obtained at 200°C. However, materials formed by hydrogen reduction are not as active as those formed using  $\text{NaBH}_4$ -reduction, because the  $\text{NaBH}_4$  reduction method may reduce only surface platinum from valence state 6 to valence state 0, but might not reduce the underlying bulk metal oxide toward the zero-valent metal. In contrast, hydrogen reduction also reduces the bulk metal oxide toward zero-valent metal, which is black. However, the resulting metal is not as catalytically active as platinum metal. As a result, the black color of those materials formed by hydrogen reduction does not correlate well with very high activity.

Economic considerations dictate that it is, of course, preferred to minimize the amount of platinum deposited, while still maintaining a suitably high level of catalytic activity. Using these production methods, platinized microporous metal oxide ceramic materials containing up to 2 or 3 % by weight platinum are preferably created, though it is more preferred that the materials have less than 1% platinum, yet more preferred for the materials to have between 0.1 and 0.6% platinum, and most preferred to have 0.3 - 0.5 % platinum by weight. Although a decrease in platinum loading is understood to reflect economic concerns, the art has heretofore been unable to produce a material loaded with a small percentage of platinum that achieves rapid and efficient catalysis such as is described in the examples below. It has been determined by the inventors that the catalytic response of the platinized metal oxide microporous materials reaches a plateau at about 0.3 - 0.5% by weight platinum. As is shown below, in the examples, it has also been determined that complete mineralization of volatile aromatic compounds can occur in a platinized microporous metal oxide nanoparticulate catalyst at 0.1% by weight platinum.

-14-

When the metal oxide pellets were titania, it was noted that the pore size distributions of the platinized materials were nearly identical to those obtained for pure titania pellets, even at platinum levels as high as 2 weight percent. The specific surface areas of platinized titania particles were about 160 m<sup>2</sup>/g after firing at 300°C for four hours. Transmission electron micrographs of these materials magnified up to 330,000 times do not indicate the presence of individual or aggregated platinum particles on the titania particles at a platinum loading of 0.3% by weight. Thus, for these conditions, the platinum appears to be highly dispersed over the surface of the titania catalyst. This conclusion is supported by the physical appearance of the platinized titania photocatalysts. The catalyst platinized with less than 0.1% by weight platinum is dark grey to black and varies from pellet to pellet. As more platinum is placed on the titania pellets, the number of grayish pellets decreases until a uniform black coating is achieved in the 0.3 weight percent platinum materials. As noted, the various reduction methods each produce materials having somewhat different blackness, although all of the methods produce blacker materials than those produced previously.

Platinized catalysts prepared according to the method of the present invention, as well as other catalysts platinized in various ways have the following characteristic colors, which can be described by reference to standard a Pantone Color Chart:

-15-

	Loading Weight % Platinum	Underlying Metal Oxide	Reduction Method	Pantone Color
5	0.5	Nanoparticulate Titania	NaBH <sub>4</sub>	Process Black 2C
	0.5	P25 Degussa Powder	NaBH <sub>4</sub>	423C
10	0.5	Nanoparticulate Titania-Zirconia (12% Zirconia)		Process Black 2C <sup>a</sup>
	2.5	Aldrich Titania Powder	Photo- reduction <sup>b</sup>	430C
	0.3	Nanoparticulate Titania	NaBH <sub>4</sub>	Process Black 2C
15	0.01	Nanoparticulate Titania	NaBH <sub>4</sub>	400C, 401C, 402C, 406C, 407C, 408C
	0.05	Nanoparticulate Titania	NaBH <sub>4</sub>	408, 409 <sup>c</sup>
20	0.1	Nanoparticulate Titania		425C

<sup>a</sup> Darker and shinier than Process Black 2C

<sup>b</sup> Prepared by National Renewable Energy Laboratory

<sup>c</sup> Particles of various colors

25 From these color data, it is apparent that at or  
below 0.05% Pt, there is insufficient Pt loaded onto  
the very-high surface nanoparticulate titania  
materials to cover all surface sites. Coverage is  
best at or above 0.1% Pt loading. It is also notable  
30 that examination in cross-section of the materials  
that appear to be fully black reveals that the black  
color is consistent even at the deepest interior  
portions of the material. Unplatinized  
nanoparticulate material is characterized as being  
35 eggshell white to light tan in color.

This method for platinizing incorporates  
improvements specific to its use with microporous

-16-

pelletized granular starting material, rather than the powdered starting material used by others. Direct application of the Sato method to the starting material used herein cannot achieve the desired uniform coating or dark black color achieved by the present inventors because the inner surfaces cannot be treated. Nor can such high specific surface area microporous materials be effectively coated in the Sato method. Likewise when the present method for platinizing is applied to standard titania powders (Degussa P-25), the characteristic black color is not observed and the catalytic activity is about two-fold lower than that observed using the materials disclosed herein.

As is shown in the non-limiting examples below, these materials are above, upon exposure to UV light, to achieve complete conversion and mineralization of both aromatic and aliphatic compounds. In the absence of UV light, these materials are sufficiently thermocatalytic to achieve complete conversion of organic material and mineralization of more than about 75% of the organic material, even at temperatures below 140°C. At higher temperatures, better mineralization ratios are observed. The striking ability of these catalysts to mineralize organics, particularly aromatics, is believed to result directly from the advantageous use of a nanoparticulate, microporous metal oxide ceramic material and from the invention of a preparation method that takes advantage of the unexpected loading properties of these materials. The method achieves uniform dispersion throughout the entire porous material while retaining high surface area and porosity. Also, it appears that the platinum does not aggregate on the catalyst surface as has been observed in other materials, but rather is highly dispersed.

-17-

The truly dispersed platinum coating of nanoparticulate materials is thought to develop because of the distinct surface arrangement of these materials compared to titania powder. Compared to the size of the platinum metal, the substrate surface of titania powder is very large. Individual platinum metal ions can attach to the substrate in a widely dispersed manner. However, because platinum is more attracted to itself than to the titania substrate, it tends to agglomerate with relatively vast uncoated spaces. Uniform coating is approached only by adding large amounts of platinum.

In contrast, the metal oxide starting materials are nanoparticulate microporous materials sintered into ceramic bodies as shown in Figs. 1-5 of U.S. Patent 5,227,342, which are incorporated herein by reference. Although these materials are solid bodies, their characteristic particulate structure reflects their formation from particulate sols. When platinum ions adsorb to these materials, the actual surface onto which platinum can migrate is small. Said another way, even though these structure materials have very high specific surface area, the surface area of each discrete surface is quite small, and is significantly smaller than a powder grain. Accordingly, an adsorbed platinum can fill an entire particle surface with very little material, yet the adsorbed platinum is not free to migrate or agglomerate because of the physical constraints of the surfaces. This is true not only at the outer particle surfaces, but also at the surfaces lining the micropores within the nanoparticulate ceramic materials. What results is a truly uniform dispersion, despite very low platinum loading levels. In contrast, when platinum can agglomerate, as on a large uninterrupted powder grain surface, uniform coating can only be achieved after sufficient

-18-

platinum has been loaded that the surface becomes, in effect, fully agglomerated. The lack of agglomerated platinum can be observed visually by TEM where the surface of the materials platinized according to the method herein disclosed, even at a magnification of 330,000.

In addition, the nanoparticulate materials have very high surface energy. In an effort to lower its surface energy, these materials are receptive to platinum binding.

The platinized microporous metal oxide materials thus produced are unique among platinized catalysts in that they couple a very high specific surface area with a highly dispersed platinum coating throughout the materials. Whereas titanium dioxide powders can have a specific surface area of about 50 m<sup>2</sup>/g, the nanoparticulate microporous materials provide much higher specific surface area both on their outer surface and through their interior. It is specifically because of these microporous inner surfaces, however, that prior methods for making platinized metal oxide catalysts are unsuitable for platinizing these starting materials.

Since much of the specific surface area is within the particles, rather than at the exterior (visible) surface, platinization by photoillumination, which reaches only the exterior surface and areas just below the exterior surface, is less efficient than the non-photoilluminating method described herein and, in fact, can never platinize the deep interior surfaces. Moreover, prior methods for platinizing at high temperatures are also not useful with the high specific surface area platinized catalyst of the present invention.

The platinized catalysts formed in the method are more desirable than existing platinized powders because the powdered materials cannot be used

-19-

effectively for gas-solid phase reactions conducted in a fixed bed reactor. Powders are generally used only to produce a slurry in a liquid phase reaction or are trapped on a support in a gas phase reaction.

5 But there is simply insufficient catalytic surface area on powders to achieve acceptable results. The combination of the reduced platinum load coupled with the high dispersion, the variety of pore sizes, and very high catalytic surface area of the platinized  
10 microporous materials make the products of the described method particularly advantageous for remediation of contaminating materials in the gaseous state. As is demonstrated below in the examples, these materials can readily mineralize organic  
15 contaminants that are generally recognized as extremely difficult to mineralize. In addition, these materials find utility as cracking catalysts, or other applications that do not require complete mineralization.

20 The platinized materials can be used in a fixed bed photoreactor as is described herein in the Examples. Alternatively, these materials can also be advantageously employed in any catalytic reactor adapted for degradation of gaseous material.  
25 Conditions for complete degradation of benzene are provided herein. One of ordinary skill will appreciate that the particular conditions appropriate for mineralizing other aromatic or complex aliphatic volatile compounds can be determined experimentally.  
30 The important conditions generally include space time (which itself depends upon reactor size and shape), water vapor and oxygen requirements, VOC concentration and catalyst amount.

35 The present invention is further clarified by consideration of the following examples which are intended to be exemplary rather than limiting.

-20-

## EXAMPLE 1

## Catalyst Preparation

Titanium dioxide particles were prepared by a sol-gel technique as previously described in U.S. Patent No. 5,227,342. Titanium tetraisopropoxide was hydrolyzed under acidic conditions and the resulting colloidal suspension was then dialyzed until the pH of the suspension was about 4. The suspended colloidal particles were between about 10 and 20 nm in size. The dialyzed sol was evaporated to form a xerogel which was heated under controlled conditions to form a microporous ceramic material. The ceramic material was then ground and sieved to obtain titanium dioxide pellets having diameters between 0.5 and 1.4 mm.

BET analysis of nitrogen sorption data for these pellets revealed typical specific surface areas of 170 m<sup>2</sup>/g and porosities of 55%, when the ceramic materials were fired at 300°C for 4 hours. The mean pore diameter for these materials was about 45 Å. X-ray diffraction analysis indicated that the crystal structure of these materials was 89% anatase and 11% rutile with the primary crystallites having an average size of about 80 Å.

The titania pellets were placed in water and were then impregnated with a dilute solution (8% by weight) of aqueous hexachloroplatinic acid (Aldrich Chemical, Catalog No. 26258-7). Sufficient platinum was used to achieve platinum loading of between 0.1% and 2% platinum by weight relative to the titania pellets. The adsorbed platinum was then directly reduced with a solution 0.3 M NaBH<sub>4</sub> in 0.01 M NaOH at room temperature. Finally, the pellets were dried at 105-110°C for 2 hours.

BET analysis demonstrated that the pore size dimensions of these platinized pellets (with up to 2% by weight platinum) were identical to those obtained

-21-

for pure titania. The specific surface area of the  
platinized titania pellets was about 160 m<sup>2</sup>/g, not  
appreciably different from the pure titania  
particles. Transmission electron microscopy (TEM),  
5 up to a magnification of 330,000, did not indicate  
the presence of individual platinum particles on the  
titania at a platinum loading of 0.3 weight percent.  
At 0.1 weight percent platinum, the catalytic  
material ranges from dark grey to black and varies  
10 from particle to particle, as reported elsewhere in  
the specification. However, at higher platinum  
loads, the number of grayish particles decreases  
until a uniform black coating is achieved at 0.3  
weight percent platinum.

15

## EXAMPLE 2

Experiments to determine the photocatalytic  
activities of the platinized materials (and their  
unplatinized counterparts) were conducted in a fixed  
bed annular photoreactor operated in a single-pass  
20 mode. This annular reactor was fabricated from  
glass, with the width of the annulus being 2-3 mm.  
The annulus surrounded a 4 W fluorescent black light  
bulb (GE F4T5-BLB) positioned along the longitudinal  
axis of the reactor. This bulb emits radiation over  
25 the range of 300-425 nm, with peak intensity centered  
at 350 nm. This reactor design was employed because  
it provides efficient utilization of that portion of  
the incident radiation that strikes the  
photocatalyst, and because it allows a relatively  
30 large amount of catalyst to be placed in the reactor.  
The illuminated catalyst is not confined to the inner  
surface of the annulus. Because of the irregular  
particle shapes, annular radiation sometimes does not  
strike the catalyst until near the outer surface of  
35 the annulus. There are even gaps where radiation can  
pass through the annular reactor. Accordingly, a

-22-

layer of aluminum foil was wrapper around the reactor to reflect some of this radiation back into the reactor. Thus, the photoactive catalyst is actually spread throughout the reactor, although the largest proportion of photoactive catalyst was located at the inner region of the annulus. The irregular distribution of photoactive catalyst increases the probability that a reactant gas will contact a photoactive surface at some time during its flow through the reactor.

Each experiment employed 19 g of platinized catalyst prepared accordingly to the method of the present invention (0.1% platinum by weight) unless otherwise noted. However, given the non-uniform sizes and shapes of the photocatalyst particles, these particles were not closely packed into the annular region of the reactor. Thus, the distribution of the catalyst within the annulus was not uniform. In addition, these materials display a high absorptivity for near-UV radiation with an energy above the band gap energy of the material. It is likely that the photoactive region of the catalyst is only a layer of about 10 microns thick at the surface of the illuminated portion of the catalyst. As a result, it is not possible to accurately estimate the amount of catalyst that is actively illuminated. Most of the photocatalyst is probably not illuminated, especially that portion that resides deep in the interior of the porous pellets.

The reactant gas, typically benzene, was delivered to the apparatus from a compressed gas cylinder in a feed stream that also included hydrocarbon-free air (less than 0.1 ppm total hydrocarbons, available from Scott Specialty Gases), zero air (21% oxygen, 79% nitrogen, available from Liquid Carbonic), oxygen (99.999%, Liquid Carbonic) and nitrogen (99.999%, Liquid Carbonic). The benzene

-23-

concentration was  $491 \text{ ppmv} \pm 2\%$ . The gas feed stream was humidified by passage through a water saturator, and the water content in the reactant stream was fixed by controlling the flow rate and the temperature of the saturator. The mole fractions of the gaseous mixture of benzene, oxygen and water vapor were  $4.9 \times 10^{-4}$ , 0.2, and 0.03, respectively. At a significantly lower water mole fraction,  $<5 \text{ ppm}$ , conversion using the unplatized catalyst was still shown to be substantially complete (at  $130^\circ\text{C}$ ), but the mineralization ratio (moles of  $\text{CO}_2$  produced per mole of input organic material converted) was in steep and rapid decline to about 3, although this could be increased to about 4, upon addition of water to the 0.03 mole fraction level. At a water mole fraction of 0.015, conversion and mineralization can be achieved. Reactor temperature was varied using heating tapes and a temperature controller (Glas Col D.T. II). The reactor was operated by starting illumination when the gas flow was started. No measurements were taken during the first 15 minutes of flow to allow the system to reach thermal equilibrium with the heat energy produced by the UV bulb.

The product stream was allowed to flow continuously from the reactor to the sampling loop of a chromatographic valve. A Hewlett-Packard 5890 gas chromatograph (Series II) equipped with a flame ionization detector (FID), a thermal conductivity detector (TCD) and a Porapak R column was employed to analyze discrete samples of the reactor effluent stream. Benzene and carbon dioxide concentrations were determined by FID and TCD, respectively. The GC was calibrated using known concentrations of benzene and carbon dioxide.

During the experiments described herein, the only carbon-containing species in the product stream

-24-

that were observed at concentrations large enough to be quantified were benzene and carbon dioxide. Other extremely small peaks were observed intermittently at concentrations below 1 ppmv, assuming an identical sensitivity of the FID for these species and benzene. Since these peaks were not observed consistently even during the performance of a single experiment, no effort was made to identify them.

## EXAMPLE 3

10                    Photocatalytic Decomposition of Benzene  
                         Over Platinized Catalyst

Using the input gas stream described above, the platinized catalysts were evaluated under steady state conditions. Steady state conditions were reached after 2 to 3 hours of UV photoillumination when the platinized titania catalyst was used. At least five hours were required to achieve a steady state using the unplatinized microporous titania membranes tested for comparison. At steady state, conversion on the unplatinized catalyst remains constant, although a gradual decrease in mineralization ratio is observed over time. This is thought to result from adsorption of some species to the catalyst that correlates with a yellowing of the unplatinized catalyst. Because of the dark color of the platinized catalyst, the presence of yellowing cannot be confirmed.

Essentially complete conversion (degradation) of benzene was obtained with the photoilluminated platinized catalyst at all operating temperatures in the measured range of 70°C to 140°C. The smallest mineralization ratio obtained with the platinized catalyst was 5.1, observed at 70°C. The highest mineralization ratio, 5.8, was obtained at temperatures of 110°C and higher. The difference in mineralization ratio between 5.8 and the

-25-

stoichiometric value of 6 can be ascribed to analytical errors in measuring the concentrations of the reactants in products as well as to possible adsorption of carbon on the surface of the platinized catalyst.

These results contrast with those obtained using the unplatinized titania starting material as the photocatalyst. Using that material, the mineralization ratio appears to be somewhat dependent upon temperature, increasing from about 3.6 to about 4.3 between the temperatures of 70°C and 140°C. Likewise, the photocatalytic conversion or degradation of benzene increases from about 60% to about 80% between 70°C and 110°C, then tapers off in slope to a maximum conversion of about 86% at 140°C.

Using the platinized catalyst at a reaction temperature as low as 70°C and a space time as low as  $1.8 \times 10^9$  g-seconds per mole in the annular reactor containing catalyst pellets, the conversion of benzene was 100% and the mineralization ratio (moles of carbon dioxide produced relative to moles of benzene converted) was above 5.0. The mineralization ratio approached the theoretical maximum of 6.0, if either the reaction temperature was increased to 110°C or if the space time was increased to greater than  $4 \times 10^9$  g-seconds per mol. By comparison, the unplatinized titania catalyst at 130°C can achieve full conversion only at space times higher than  $2.2 \times 10^9$ . At that condition, however, the mineralization ratio is near a plateau of less than 4.4.

#### EXAMPLE 4

##### Effect of Oxygen on Conversion and Mineralization Using Platinized Titania Catalyst

The effect of oxygen on both conversion and mineralization of benzene was determined by

-26-

performing the photocatalytic reaction at various mole fractions of oxygen between 0.1 and 0.6 on 0.1 weight percent platinum titania catalyst at 70°C. The mole fractions of benzene and water vapor were  $2.5 \times 10^{-4}$  and  $1.5 \times 10^{-2}$ , respectively. The space time was  $1.9 \times 10^9$  gram-seconds per mol. The results indicated that conversion is sensitive to the concentration of oxygen only when the mole fraction of oxygen in the gaseous reactant stream is lower than 0.2. At higher than 0.2 mole fraction, conversion is essentially 100%. However, the mineralization ratio clearly increases as the mole fraction of oxygen increases up to a mole fraction of 0.4. The optimum mole fraction of oxygen for the mineralization of benzene to carbon dioxide was between about 0.4 and 0.55, with a maximum at about 0.45. The reason for the observed decrease in mineralization ratio at mole fractions of oxygen greater than 0.55 is not known.

## EXAMPLE 5

## Comparative Thermal Catalytic Oxidation of Benzene

A series of experiments were performed to directly compare the thermal catalytic activity of platinized titania catalysts prepared in accordance with the present method against other platinized catalytic material. Catalyst was placed in a tubular reactor surrounded by four 4W UV lights (GE). The tubular reactor was coated with foil so that only thermal, but not light effects were measured. In these experiments, which are intended only as demonstrations of the superiority of the claimed materials, starting materials and reduction conditions were compared directly. Results are reported in Table 1.

Platinized titania pellets, at 0.3% and 0.5% by weight platinum, were prepared according to the

-27-

sodium borohydride reduction method of the present invention. In addition, Degussa P25 powder was compressed into pellets comparable in size to those of the starting materials of the present method, and were either platinized to 0.5 weight percent using  $\text{NaBH}_4$  reduction, or were platinized to 0.3 weight percent by  $\text{H}_2$  reduction at  $200^\circ\text{C}$ . Finally, mixed titania-zirconia and titania-silica pellets were platinized to 0.5 weight percent platinum according to the method of the present invention. The mixed oxide starting materials were prepared according to the modified method of Anderson and Xu. Separate Zr and Ti sols were prepared and then mixed together. The mixed sol, formed of separate Zr and Ti particles, was not roto-evaporated, but was dried in an oven as described above. The xerogel thus formed was fired to form a mixed oxide ceramic material which was crushed and platinized as described herein. The resulting material had a mean pore diameter of  $35\text{\AA}$ . Also used in these experiments was commercially available 5894 industrial grade thermal catalyst (Union Carbide).

The following conditions were employed. Benzene, at a concentration of 509 ppm was introduced into the tubular reactor with oxygen gas at a molar ratio of 0.2, the remainder being nitrogen, water vapor being present at less than 5 ppm. The feed stream flow rate was 20 ml/minute. The weight of each catalyst tested was 0.407 g. Unless otherwise noted, the reaction time was about 20 hours.

-28-

TABLE 1

Catalyst	Reduction Method	CO <sub>2</sub> Production Rate (mol CO <sub>2</sub> /s·gPt)	[CO <sub>2</sub> ] Produced	Apparent Turnover Number (mol C <sub>6</sub> H <sub>6</sub> /s·gPt)
0.3% wt Pt/TiO <sub>2</sub>	NaBH <sub>4</sub>	2.6 x 10 <sup>-6</sup>	238 ppm	5.2 x 10 <sup>-7</sup>
0.5% wt Pt/TiO <sub>2</sub>	NaBH <sub>4</sub>	2.4 x 10 <sup>-6</sup>	357 ppm	4.9 x 10 <sup>-7</sup>
0.3% wt Pt/P-25	H <sub>2</sub> at 200°C	0	0	0
0.5% wt Pt/P-25	NaBH <sub>4</sub>	8.5 x 10 <sup>-7</sup>	127 ppm	2.6 x 10 <sup>-7</sup>
0.5% wt Pt/TiO <sub>2</sub> -ZrO <sub>2</sub>	NaBH <sub>4</sub>	2.6 x 10 <sup>-6</sup>	386 ppm	5.3 x 10 <sup>-7</sup>

The conversion percent and mineralization ratio for catalytic oxidation of benzene were also determined for various platinized catalysts. Table 2 demonstrates the clear superiority of catalysts prepared on microporous, nanoparticulate substrates as opposed to other commercial platinized catalysts. Note that these reactions were not intended to represent optimal oxidation conditions, but rather to provide a rapid comparison of various catalysts. Accordingly, the reactions were run for a short time, at a high flow rate using a small amount of catalyst. Therefore, these reactions were not run under conditions where one would expect complete conversion; yet, under these conditions the materials of the present invention exhibit mineralization ratios between 5 and 6, reflecting almost complete mineralization of the converted benzene. Under more typical reaction conditions, complete mineralization and conversion would therefore be expected.

TABLE 2

Catalyst	Reduction Method	Conversion (percent)	Mineralization ratio
0.3% wt Pt/TiO <sub>2</sub>	NaBH <sub>4</sub>	9.1	5.2
0.5% wt Pt/TiO <sub>2</sub>	NaBH <sub>4</sub>	14.5	4.9
0.5% wt Pt/TiO <sub>2</sub> -ZrO <sub>2</sub>	NaBH <sub>4</sub>	15.4	4.9
0.5% wt Pt/TiO <sub>2</sub> (P-25)	NaBH <sub>4</sub>	7.5	3.4
0.3% wt Pt/P-25	H <sub>2</sub> gas at 200°C	0	--
5894-Industrial (.16%Pt)	unknown	0	--

The catalytic oxidation of ethylene was also monitored using the various catalysts. In this

-29-

experiment, reported in Table 3, oxygen was present in the feed stream at 0.045 molar ratio, ethylene gas was present at the indicated concentration, the flow rate was 60 ml/minute and water vapor was present at less than 5 ppm. The temperature was 105-106°C and 0.41 g of each catalyst was tested. Markedly better catalytic activity was observed using the materials of the present invention. With these materials, at 105°C, 50% conversion of ethylene or greater, preferably 75% conversion or greater, and most preferably 90% conversion or greater is expected. Likewise, apparent turnover numbers of  $10^{-5}$  or higher for ethylene are also characteristic. Comparable results will be observed at other temperatures.

15

TABLE 3

Catalyst	Reduction Method	C <sub>2</sub> H <sub>4</sub> (ppm)	Conversion (percent)	Apparent Turnover Number
0.3% wt Pt/P-25	H <sub>2</sub> gas at 200°C	389	1.3	$1.7 \times 10^{-7}$
0.3% wt Pt/TiO <sub>2</sub>	NaBH <sub>4</sub>	391	99.4	$1.3 \times 10^{-5}$
5894-Industrial (.16%Pt)	unknown	381	6.9	$1.6 \times 10^{-6}$

20

The data of the preceding tables demonstrates the superior ability of the materials prepared in accordance with the present invention to convert and mineralize organic materials. It further demonstrates the superior turnover rates that these materials provide. Also shown is the unexpectedly good results observed when the method of the present invention is applied to nanoparticulate microporous starting materials, as well as the fact that when other starting materials are used in the present method, the platinized materials obtained are about 50% less catalytically active.

30

**EXAMPLE 6**

35

**Catalytic Properties of Platinized Nanoparticulate  
Microporous Ceramic Materials**

Platinized and unplatinized materials prepared according to the method of the present invention were evaluated separately both in terms of conversion and

-30-

mineralization under photothermocatalytic and catalytic conditions using the annular reactor.

With respect to the unplatinized titania catalysts, conversion of benzene is about 60% lower in the absence of UV illumination across the temperature range 70-140°C. At its maximum, the unplatinized material exhibits about 25% conversion at 140°C. However, across the entire temperature range, the mineralization ratio of the unplatinized material is constant at less than 1.5.

In striking contrast, however, the applicants have here determined that the platinized catalyst prepared according to the method of the present invention is very catalytic. In the complete absence of UV illumination, these materials (0.1%wt Pt) exhibit complete conversion of benzene at temperatures as low as 130°C. Moreover, a sharp upward-rising slope is observed in the temperature range between 90 and 130°C. Over this interval, conversion increases from about 10% to 100%. Likewise, over this same temperature range, the mineralization of benzene increases from a ratio of about 1 at 90°C to greater than 4.5 at 130°C. It is concluded from these observations that platinizing the titania catalyst promotes both the photocatalytic and thermocatalytic reactions. Moreover, the ability to complete convert benzene and to achieve almost complete mineralization at temperatures below 140°C is believed to be unique among platinized catalysts. Typically, catalytic converters operate with maximal efficiency at higher temperatures such as 200°C to 600°C, depending upon the chlorination of the compounds converted. What these platinized materials offer, then, is an opportunity to provide efficient catalytic conversion at lower temperatures, thereby permitting the conversion of toxic emissions from vehicles, such as automobiles and trucks, at temperatures where no such

-31-

conversion can now take place using existing catalytic converters. This observation can translate directly into reduced toxic emissions.

5 It is also noteworthy that since these catalytic materials can be made to operate with almost equal efficiency in the presence or absence of UV photoillumination, a significant cost reduction can be obtained by eliminating the need for photoillumination entirely, relying exclusively on thermocatalysis for  
10 conversion and mineralization of toxic materials such as benzene. This is particularly attractive, since uniform temperature control can readily maintain the catalytic material at a uniform temperature, thus allowing catalytic activity throughout the microporous  
15 materials. In contrast, it has already been noted that photoillumination of these materials is necessarily less than 100% efficient since UV illumination cannot pass entirely into the interior of the pelletized ceramic bodies.

20 Complete conversion or mineralization is not required of a process using the disclosed platinized materials. The materials themselves are capable of promoting both high conversion and high mineralization rates. However, in any particular application, even  
25 partial conversion or mineralization may be sufficient, particularly when toxic intermediates are not produced or are produced in small amounts as products of conversion. Moreover, for certain materials even moderate conversion and mineralization  
30 can represent dramatic improvement over prior catalytic processes. In such cases, the improved activity of the disclosed materials is itself sufficient to merit their use in such remedial processes.

35 These platinized materials have been successfully used at 70°C to completely mineralize xylene (100 ppm in the feed stream) and methylene chloride (100 ppm in

- 32 -

the feed stream), in addition to the other compounds described herein.

The present invention is not intended to be limited to the embodiments described in the examples,  
5 but rather to encompass all such modifications and variations as come within the scope of the following claims.

-33-

## CLAIMS

1. A method for forming a platinized microporous metal oxide ceramic catalyst, the method comprising the steps of:

5 providing a microporous nanoparticulate ceramic metal oxide material having micropores in the interior thereof with a mean pore diameter of less than 100 Å, the material having an available surface area of between 50 and 500 m<sup>2</sup>/g;

10 adsorbing a platinum precursor onto the microporous material without photo-illumination, at a temperature between room temperature and 200°C for a time sufficient to achieve steady-state adsorption of the platinum precursor;

15 reducing the adsorbed platinum precursor to zero valent platinum metal on the microporous material at a temperature that does not affect the mean pore diameter of the microporous material and at a pH that does not dissolve the microporous material; and

20 drying the platinized microporous material at a temperature that does not affect the mean pore diameter of the material to form a platinized microporous metal oxide catalyst.

25 2. A method as claimed in Claim 1 wherein the catalyst is capable, under photoillumination at a temperature of 70°C, of complete conversion of an input stream of benzene gas, with a mineralization ratio of greater than 5.

30 3. A method as claimed in Claim 1 wherein the catalyst can achieve, at a temperature of 105°C, greater than 50% conversion of ethylene with an apparent turnover number of 10<sup>-5</sup> or greater.

-34-

4. A method as claimed in Claim 1 wherein the adsorbing step comprises mixing the microporous material with hexachloroplatinic acid for less than about one hour at room temperature.

5 5. A method as claimed in Claim 1 wherein the reducing step comprises soaking the platinum-adsorbed material in a basic solution comprising 0.1 - 0.3 M sodium borohydride at room temperature.

10 6. A method as claimed in Claim 1 wherein the reducing step comprises exposing the platinum-adsorbed material to H<sub>2</sub> gas at a temperature between room temperature and about 200°C.

15 7. A method as claimed in Claim 1 wherein the microporous material is titania having dimensions ranging in size from 0.05 mm to 10 mm.

8. A platinized catalyst comprising:  
a microporous nanoparticulate ceramic metal oxide material having micropores in the interior thereof with a mean pore diameter of less than 100 Å, the  
20 material having an available surface area of between 50 and 500 m<sup>2</sup>/g; and  
a platinum coating uniformly dispersed on the available surface area.

-35-

9. A platinized catalyst as claimed in Claim 8  
wherein the catalyst can achieve, under  
photoillumination at a temperature of 70°C, complete  
conversion of an input stream of benzene gas, with a  
5 mineralization ratio of greater than 5.

10. A platinized catalyst as claimed in Claim 8  
wherein the catalyst can achieve, without  
photoillumination at a temperature below 140°C,  
complete conversion of an input stream of benzene gas,  
10 with a mineralization ratio of greater than 4.5.

11. A platinized catalyst as claimed in Claim 8  
wherein the catalyst can achieve, at a temperature of  
105°C, greater than 50% conversion of ethylene with an  
apparent turnover number of  $10^{-5}$  or greater.

12. A platinized catalyst as claimed in Claim 8  
wherein the platinum comprises less than 0.6% by  
weight of the weight of the metal oxide.

13. A platinized catalyst as claimed in Claim 8  
wherein the platinum comprises between 0.1% and 0.3%  
20 by weight of the weight of the metal oxide.

14. A method for remediating an organic compound  
in the gas phase without photoillumination, the method  
comprising the steps of:  
providing a microporous nanoparticulate ceramic  
25 metal oxide material having micropores in the interior  
thereof with a mean pore diameter of less than 100 Å,  
the material having an available surface area of  
between 50 and 500 m<sup>2</sup>/g;

-36-

adsorbing a platinum precursor onto the microporous material without photo-illumination, at a temperature between room temperature and 200°C for a time sufficient to achieve steady-state adsorption of the platinum precursor;

reducing the adsorbed platinum precursor to zero valent platinum metal on the material at a temperature that does not affect the mean pore diameter of the microporous material and at a pH that does not dissolve the microporous material;

drying the platinized microporous material at a temperature that does not affect the mean pore diameter of the material to form a platinized microporous metal oxide catalyst; and

exposing the catalyst to an input stream of the organic compound in the gas phase at a temperature and for a time sufficient to completely convert the organic compound and to achieve at least about 75% mineralization.

15. A method as claimed in Claim 14 wherein the catalyst is exposed to the input stream without photoillumination.

16. A method as claimed in Claim 14 wherein the catalyst is exposed to the input stream at a temperature below 140°C.

17. A method as claimed in Claim 14 wherein the catalyst is capable, without photoillumination at a temperature below 140°C, of complete conversion of an input stream of benzene gas, with a mineralization ratio of greater than 4.5

-37-

18. A method as claimed in Claim 14 wherein the catalyst is capable, under photoillumination at a temperature of 70°C, of complete conversion of an input stream of benzene gas, with a mineralization  
5 ratio of greater than 5.

19. A method as claimed in Claim 14 wherein the catalyst can achieve, at a temperature of 105°C, greater than 50% conversion of ethylene with an apparent turnover number of  $10^{-5}$  or greater.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/08471

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :B01J 23/00, 23/40; C07B 63/00 US CL :502/325, 326, 349, 350; 204/158.21 According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 502/325, 326, 349, 350; 204/158.21, 158.2; 423/437R Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	EP, A, 633064-A1 (MURASAWA ET AL) 11 January 1995, page 4, lines 22-39.	1-13		
Y	WO, A, 92/08544 (YUE ET AL) 11 December 1991, page 6, lines 18-26; page 7, lines 4-7.	1-13		
Y	Journal De Chimie, volume 5, No. 12-1981, 07 August 1981, Pichat et al, "Photocatalytic Hydrogen Production From Aliphatic Alcohols over a Bifunctional Platinum on Titanium Dioxide Catalyst", pages 627-636, especially page 628.	1-13		
Y	Journal of Catalysis 92, 11-16, 25 April 1984, S. Sato, "Photoelectrochemical Preparation of Pt/TiO <sub>2</sub> Catalysts", pages 11-16, especially page 13.	1-13		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.				
<table border="0"> <tr> <td>           * Special categories of cited documents:            "A" document defining the general state of the art which is not considered to be of particular relevance            "E" earlier document published on or after the international filing date            "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            "O" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but later than the priority date claimed         </td> <td>           "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention            "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone            "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art            "Z" document member of the same patent family         </td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
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Date of the actual completion of the international search		Date of mailing of the international search report		
06 AUGUST 1996		30 SEP 1996		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231		Authorized officer <i>M. P. Dang</i> THUAN DANG		
Facsimile No. (703) 305-3230		Telephone No. (703) 308-0661		

**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US96/08471**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,449,443 (JACOBY ET AL) 12 September 1995, column 3, lines 40-68; column 4, lines 57-64.	14-19
Y	US, A, 5,032,241 (ROBERTSON ET AL) 16 July 1991, column 1, lines 8-40.	14-19
Y	US, A, 5,252,190 (SEKIGUCHI ET AL) 12 October 1993, column 1, line 25; column 2, lines 49-55; column 4, lines 31-33	14-19